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(54) **Process for the production of oxyacids from carbohydrates**

Verfahren zur Herstellung von Sauerstoffsäuren aus Kohlenhydraten

Méthode de préparation d'acides contenant de l'oxygène à partir d'hydrates de carbone

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30, 1926, pages 939 - 953; **C.C. PALIT ET AL.:**
'CATALYTIC AND INDUCED OXIDATION OF
SOME CARBOHYDRATES, URIC ACID, AND
INORGANIC SUBSTANCES.'

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

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EP 0 548 399 B1

Description

The present invention relates to a process for the production of hydroxyacids from carbohydrates, by catalytic oxidation with an oxygen-containing gas.

It is known to prepare polyhydroxycarboxylic acids by oxidation of saccharides and/or polysaccharides by means of electrochemical oxidation in the presence of CaBr_2 or by means of chemical oxidising agents such as potassium permanganate, persulphates, sodium hypobromite or hypochlorite, and periodate. Such known processes have drawbacks deriving from the use of expensive and toxic reagents and furthermore deriving from a contamination of the reaction products with the oxidising chemicals. In this connection, the presence of bromine or chlorine or compounds thereof in the oxidation products is susceptible to highly effect the biodegradability properties of the obtained hydroxyacids.

Also known are methods of catalytic oxidation of carbohydrates with use of molecular oxygen, which indeed constitutes a very desirable oxidising agent in view of its low cost and for environmental reasons.

In this connection, DE-B-2,123,621 describes a process for the production of aldonic acids by catalytic oxidation of sugar alcohols, which do not contain free aldehyde or ketone groups, with oxygen or with an oxygen containing gas, in an alkaline medium, in the presence of a noble metal catalyst, particularly platinum or palladium.

EP-A-0 232 202 describes a process for the oxidation of water soluble saccharides to polyhydroxycarboxylic acids with molecular oxygen in an alkaline medium in the presence of a noble metal catalyst bound to an inert support, wherein the catalyst is doped with a metal of groups IV, V or VI of the periodic table, particularly Pb or Bi.

US-A-3873614 describes a method for preparing dicarboxylic derivatives of carbohydrates by oxidation of the carbohydrates in an aqueous alkaline medium containing catalytic amounts of a heterogeneous catalyst formed of silver oxide or mixtures of silver oxide and an oxide of metals, such as copper, cobalt and iron.

The above mentioned processes make use of expensive catalysts which require regeneration.

US-A-3736224 disclosed a method for bleaching cellulosic materials under the action of oxygen in an alkaline medium in the presence of catalytic amounts of copper oxide.

In view of the above state of the art, it is an object of the present invention to provide a new method of oxidation of carbohydrates, which is inexpensive and advantageous as regards the reagents used in the method.

A further object is to provide a method which, with the particular reference to the oxidation of starches and starch hydrolyzates, gives rise to an oxidation product with improved biodegradability properties. These and other objects which will be apparent from the description, are achieved by a method for the production of hydroxyacids from carbohydrates by catalytic oxidation with an oxygen-containing gas, in an alkaline medium, characterised in that the oxidation is carried out by homogeneous catalysis in the presence of a catalytic amount of an ion of a transition metal selected from the group consisting of Cu, Cr, Co, Ni, Fe, V, Ti, Mn and mixtures thereof, wherein the carbohydrate is first dissolved or dispersed in an aqueous medium with the addition of a catalytic amount of said metal ion and then an amount of base is added such as to maintain the pH in alkaline conditions throughout the oxidation reaction and through said medium molecular oxygen is fed, provided that when the reaction is carried out in the presence of Cu, Co, Ni or Fe ions the aqueous medium does not contain any amine compound that acts as a ligand for such ions.

Carbohydrates, which constitute the substrate to which the oxidation method of the invention is applied, include:

- monosaccharides such as natural pentoses and hexoses, particularly arabinose, glucose, fructose, and reduced monosaccharides, such as sorbitol, mannitol, erythritol, arabitol;
- disaccharides, such as maltose, saccharose, cellobiose, lactose and trehalose, and
- polysaccharides, particularly dextrans, dextrins, starch hydrolyzates, starch and cellulose.

The term starch is meant to include all starches and starch derivatives which are soluble in water or which may be solubilized or dispersed in water e.g. by addition of alkali or alkaline-earth metal hydroxides. The term starch therefore also includes amylose and amylopectin and starches having high amylose content, such as amylo maize and starches having high amylopectin content such as waxy starch. Native starches extracted from various plants such as potato, rice, tapioca, maize and cereals are preferred particularly maize and potato starch.

Hydrolysis products of starch are constituted by mixtures of oligomers with various numbers of glucoside units, including glucose monomer. These starch hydrolyzates are easily obtainable, for example, by enzymatic hydrolysis, preferably with the use of endoenzymes.

It is believed that the active catalyst in the reaction is a complex between the anionic form of the substrate and the metal ion in homogeneous phase.

The metal ion is introduced into the aqueous medium by means of a salt thereof, preferably a sulphate or a chloride; the preferred metal ion is copper.

Typically, the metal ion concentration in the reaction medium is in the range of from 0.1×10^{-2} to 4×10^{-2} M.

The preferred bases, for use in the process of the invention, are alkali and alkaline earth metal hydroxides, particularly sodium hydroxide and calcium hydroxide, amines such as ethylamine, diethylamine, triethylamine, and ammonia or quaternary ammonium hydroxides. Basic salts may also be used, such as sodium carbonate and bicarbonate, provided that they are added in an amount such as to achieve the desired alkaline conditions. The alkaline agent is added to the reaction medium in a concentration such as to obtain an initial pH in the range of from 7.5 to 14; preferably from 8 to 13 and such as to maintain alkaline conditions throughout the reaction and neutralize the hydroxyacids which constitute the reaction product.

The oxidation reaction is carried out by bubbling molecular oxygen through the alkaline medium, typically at a temperature of from 20 to 100°C. Air may be used as the source of molecular oxygen. The oxygen partial pressure may typically range from 0.02 to 10 MPa, the higher limit being dictated by economical reasons.

Oxidation of polysaccharides

Polysaccharides, as above defined, constitute a preferred substrate to which the process of the invention is applied.

It is believed that the process of the invention, when applied to cellulose, starch and starch hydrolyzates, provides a novel oxidation product which is endowed with improved properties, particularly improved biodegradability, which makes such product particularly useful for several applications, which will be seen in more detail in the following. Such oxidation products, as obtainable by the process of the invention, constitute, therefore, a further subject of the invention.

The content of polysaccharides in the aqueous medium is generally between 10 to 40% wt (dry basis), preferably 10 to 30% wt.

The oxidation of starch by molecular oxygen is preferably carried out at a temperature higher than that of starch gelatinization in the alkaline medium; under gelatinization conditions the viscosity of the medium is very high and intensive mixing is required. In this connection pre-gelatinized starch is preferably used.

During the first 30-40 minutes of reaction, the rate of hydroxyacid formation is low due to poor mixing; however, the formation of carboxy groups (practically one COOH group per each 50-100 glucoside rings) lowers the viscosity of gelatinized material and increases solubility, so that the reaction may take place throughout all the reaction medium.

It is believed that the oxidation reaction proceeds initially with oxidation only of secondary hydroxy groups by cleavage of C-C bonds; the primary hydroxy groups appear to be more stable to oxidation as it can be proved by a comparison of the rates of starch and dextran oxidation. The latter contains only few primary OH groups (as compared to starch), nevertheless the rate of dextran oxidation is somewhat higher than that of starch oxidation in the same conditions.

Preferred conditions for the oxidation of starch, cellulose, starch hydrolyzates, dextrans and dextrans are a temperature in the range of from 50 to 80°C and pH of from 8 to 13 which is maintained throughout the reaction process.

By operating at these conditions, the undesirable degradative oxidation of the formed hydroxyacids with formation of CO₂, formic acid and low-molecular weight hydroxyacids, is avoided. Also avoided is the formation of aldehydes, side products and their poly condensation which would lead to the formation of coloured products.

At the end of the process the reaction medium consists of an aqueous solution or suspension of salts of hydroxyacids which are stable at pH 5-14 and are easily hydrolyzed in stronger acidic solutions with the formation of unstable acids which decompose quickly with formation of formic acid.

The catalyst can be removed from the reaction product by means of cationic resins, particularly sulphonic resins in the form of the sodium salts and aminodiacetic resins.

Example 1

In a glass reactor having a volume of 1.5 l provided with a mechanical stirrer, oxygen diffuser and thermostatic jacket, 0.8 l of water, 0.2 kg of maize starch and 2.6 g copper sulphate (CuSO₄ · 5H₂O) (copper ion concentration equal to 1×10^{-2} M), are introduced and then the stirrer is switched on at high revolution. Stirring is continued for about 2-3 minutes, until complete dissolution of the copper salt.

25 g of granular KOH (85% wt) are added and oxygen is introduced into the reaction volume through the diffuser at a rate of about 100ml/min. At the temperature of about 60°C the starch suspension begins to gelatinize, mixing becomes more difficult and stirring power is increased. After gelatinization, the temperature is further increased to 80°C and maintained constant.

After 30 minutes of stirring at 80°C in the oxygen atmosphere, there is a strong reduction of the viscosity of the gelatinized starch, due to the partial oxidation of the alcoholic groups to carboxylic groups; the effectiveness of stirring is further increased. After two hours from the beginning of the reaction at 80°C, the reaction stops as the result of complete neutralization of the hydroxyacids which are formed as the result of starch oxidation. At the end of the process (pH of about 8) the reaction products contain potassium salts of hydroxyacids at a concentration of about 0.3 M ex-

pressed as moles of carboxylic group in solution.

The results are summarised in table 1.

Examples 2-5

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The procedure of example 1 was repeated with the use of different starch substrates and dextran.

The conditions for each of examples 2-5 and the obtained results are summarised in table 1.

Examples 6-9

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The procedure of example 1 was repeated by using different metal ions as catalysts, by subjecting to oxidation with molecular oxygen the hydrolyzate of amylopectin starch (molecular weight MW. of about 10^5) at 75°C, with the use of sodium hydroxide as the base at a molar concentration in the reaction medium of 0.2 M.

The reaction conditions and the results are summarised in table 2.

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TABLE 1
OXIDATION OF POLYSACCHARIDES WITH O₂

Ex	substrate	g/l	catalyst	conc (M)	Base concentration		T(°C)	reaction time (h)	Hydroxides concentration (M)	
					g/l	M				
1	Maize starch	200	CuSO ₄	1·10 ⁻²	KOH	25	0.37	80	2	0.30
2	Potato starch	200	CuSO ₄	1·10 ⁻²	Ca(OH) ₂	50	0.65	95	6	1.10
3	Sorghum Starch	250	CuCl ₂	1·10 ⁻²	NaOH	28	0.70	75	5	0.65
4	Maize starch	200	CuSO ₄	1·10 ⁻²	NH ₄ OH	-	0.60	80	12	0.25
5	Dextran (M.W.~10 ⁷)	50	Cu(CH ₃ COO) ₂	5·10 ⁻²	NaOH	10	0.25	75	8	0.22

TABLE 2
OXIDATION OF THE HYDROLYZATE OF AMYLOPECTIN STARCH ($MV \sim 10^5$) AT 75°C WITH NaOH 0.2 N

Ex	Catalyst	conc (M)	Oxygen flow rate moles/sec	reaction time (h)	ΔO_2 moles	Hydroxyacid concentration M
6	$CuSO_4 \cdot 5H_2O$	$1 \cdot 10^{-2}$	$4.0 \cdot 10^{-5}$	2	0.15	0.19
7	$FeSO_4 \cdot 7H_2O$	$1 \cdot 10^{-2}$	$2.3 \cdot 10^{-5}$	5	0.025	0.06
8	$Cr(NO_3)_3 \cdot 9H_2O$	$1 \cdot 10^{-2}$	$1.5 \cdot 10^{-5}$	5	0.06	0.14
9	$Co(CH_3COO)_2$	$1 \cdot 10^{-2}$	$2.0 \cdot 10^{-5}$	3	0.09	0.17

ΔO_2 = moles of consumed oxygen

Example 10

The oxidation of cellulose was carried out in the glass reactor of example 1 provided with a thermostatic jacket and mechanical stirrer. Air was bubbled through the reaction medium throughout the overall oxidation process at atmospheric pressure.

100 g of microcrystalline cellulose, 3 g copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 900 ml water were introduced into the reactor and 25 g NaOH were added subsequently and the temperature was maintained at 70°C. The reaction was carried out for 20 hours.

At the end of the reaction a heterogeneous solution was obtained:

content of non-dissolved cellulose: 50 g;

weight of the soluble fraction of the oxidized reaction product: 50 g;

content of carboxylic groups; 1 COOH group per each 2 glucosidic unit; the concentration in solution of the carboxylic groups was equal to about 0.17 molar (M).

Example 11

Under the same conditions of example 10, oxidation of cellulose was carried out with molecular oxygen. The substrate which was used, was a cellulose obtained by treatment of acetyl-cellulose with a NaOH solution, in order to hydrolyze the acetyl esters, which was then washed with distilled water and dried in air.

The oxidation of the hydrolyzed acetyl-cellulose (10% wt) was carried out in the presence of NaOH 0.1 N (3.6 g of NaOH in solution). The oxidation of cellulose stops after neutralization of the base by the formed hydroxyacids.

The oxidized product includes water-soluble cellulose derivatives and non-water soluble cellulose derivatives. Table 3, hereinafter, provides the per cent amount of the water soluble fraction of oxidized cellulose.

Examples 12-15

The oxidation of hydrolyzed acetyl-cellulose was carried out according to the procedure of example 11, by changing the concentration of alkali in solution. The reaction conditions and results of examples 12-15 are summarised in table 3.

TABLE 3

OXIDATION OF SUSPENSIONS OF HYDROLYZED ACETYL-CELLULOSE (10% WEIGHT) IN WATER				
Examples	NaOH (M)	ΔO_2 * (moles)	Time of reaction (h)	Water-soluble fraction %
11	0.1	0.06	6	7
12	0.3	0.14	9	15
13	0.5	0.30	10	23
14	0.7	0.37	10	30
15	0.9	0.45	10	40

* ΔO_2 = moles of consumed oxygen

The kinetic curves of oxygen uptake during the oxidation of cellulose under the conditions of examples 11-15 are shown in figure 1.

The products of oxidation of starch, starch hydrolyzates, cellulose, dextrans and dextrans may conveniently be used as a binder for paper, as a builder for detergents, as a polyelectrolyte coalescing agent in formulations for paints and printing inks, as a high molecular weight coalescent and, as a soil removing agent in detergent compositions. The use of the oxidized starch or starch hydrolyzates as a builder for detergents is particularly advantageous in view of their improved biodegradability properties with respect to the products obtained by oxidation with hypochlorite.

Oxidation of mono- and disaccharides

Monosaccharides, reduced monosaccharides and disaccharides, as above defined, constitute a further substrate to which the process of the invention may be advantageously applied:

The oxidation is carried out in an aqueous alkaline medium with a concentration of the substrate preferably in the range of from 10 to 50% wt. The temperature of the reaction medium may vary in a wide range and is generally comprised between 25 and 80°C preferably between 45 and 65°C.

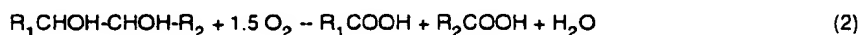
Copper salts constitute the preferred source for the catalyst ion. The nature of the anion in the copper and the

valence state of copper ions (cupric or cuprous salts) do not generally influence the rate of the process and the product ratio in the course of reaction.

The complexes of the anionic form of the substrate with metal ions are formed in the reaction medium practically instantaneously after addition of the base to the water solution of polyols containing the catalyst salt. With the use of metal salts as the catalyst, in order to avoid formation of insoluble metal hydroxides, it is always necessary to add the base to the preliminary prepared solution containing besides the metal salts also the substrate. As the base, it is possible to use the same compounds which have been mentioned hereinbefore in connection with the oxidation of polysaccharides; sodium hydroxide, potassium hydroxide and calcium hydroxide are preferred.

Degradative oxidation of the substrate is to be carefully avoided; in this connection the pH throughout the reaction medium is preferably maintained in the range of from 12 to 7.5.

The equivalent ratio of oxygen consumed and COOH groups formed in the course of the reaction is equal to about 1.5:1.0. This is in a good agreement with the reaction mechanism according to which the main reaction pathway is the interaction of oxygen with secondary hydroxy-groups and this interaction leads to cleavage of C-C bonds and formation of two carboxylic groups:



The chemical analysis of the reaction mixture shows that the main products of sorbitol and mannitol oxidation are glycolic, glyceric acids and some other high molecular weight hydroxyacids. Hydroxyacids are the primary products of saccharose oxidation.

The oxidation product of mono- and di-saccharides finds useful applications as such as a corrosion inhibitor agent and food preservative agent.

Examples 16-19

Oxidation of maltose was carried out in 0.5 l reactor provided with a mechanical stirrer, oxygen diffuser and thermostatic jacket, 20 g of maltose, 0.11 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.1×10^{-3} M), 400 ml distilled water and then 2.5 ml of NaOH 1N (to pH 9) were added under stirring at 60°C. At this temperature oxygen was bubbled through the diffuser in the reaction medium. The reaction was monitored by base consumption; base having to be added to maintain the pH at 9 due to the neutralization of the generated carboxylic groups.

The above described procedure was repeated four times, stopping each reaction after addition of increasing pre-established amounts of the base, thereby to obtain four products at different degree of oxidation (cf. Table 4). The products were recovered by removing the water by distillation under vacuum at 40°C. C^{13} NMR spectra for each of the obtained products (figures 3, 4, 5 and 6) compared with the C^{13} NMR spectrum of the starting material (figure 2) show the typical modification of the original chemical structure:

- the anomeric region (105-95 ppm) presents three new signals whose intensity increases with the degree of oxidation;
- new signals appear in the carbonyl region, 190-160 ppm (figure 7) including those of formic (af) and glycolic (ag) acids;
- the remaining part of the spectrum shows strong modifications.

TABLE 4

OXIDATION OF MALTOSE AT 60°C			
Example	mmoles of substrate	NaOH mmoles consumption	reaction time (h)
16	55.5	55.5	2.5
17	55.5	127.5	4.5
18	55.5	166.5	7
19	55.5	310.8	16

Example 20

Oxidation of saccharose is carried out in the reactor of Example 1. 100 g of saccharose, 900 ml of H_2O and 1.7 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentration in the solution $1 \cdot 10^{-2}$ M) are introduced in the reaction and are added under stirring at 75°C. At this temperature 8 g of NaOH are added (concentration 0.2 M) and oxygen is bubbled through the reaction medium through the diffuser. The reaction is monitored by oxygen and base consumption.

The reaction stops after complete neutralization of the base by the hydroxyacids which constitute the reaction product; at the end of process the pH is about 8 with a reaction time of 4 hours. The concentration of hydroxyacids (glycolic acid, glyceric acid and higher molecular weight hydroxyacids) is determined by titration and chromatography by means of an ion exchange resin PARTISIL-sax. The overall hydroxyacids concentration is 0.18 M. Together with the hydroxyacids at the end of the reaction there is a small formation of sodium carbonate and of the sodium salt of formic acid in an amount not higher than 10% with respect to the total amount of the hydroxyacids.

The results are summarised in table 5.

Examples 21-25

The procedure of example 10 is repeated with the use of different metal ion catalysts and with the use of air as oxygen containing gas (example 21); the reaction conditions and hydroxyacid concentrations found in the reaction product are summarised in table 5.

TABLE 5
OXIDATION OF SACCHAROSE AT 75°C

Ex.	Catalyst	Oxygen flow rate moles/sec	reaction time (h)	ΔO_2 moles	hydroxyacid concentration M
20	$CuCl_2 \cdot 2H_2O$	$1.4 \cdot 10^{-5}$	4	0.15	0.18
21 (X)	$CuCl_2 \cdot 2H_2O$	----	10	----	0.16
22	$FeSO_4 \cdot 7H_2O$	$0.1 \cdot 10^{-5}$	10	0.02	0.04
23	$Cr(NO_3)_3 \cdot 9H_2O$	$0.9 \cdot 10^{-5}$	6	0.06	0.13
24	$Co(CH_3-COO)_2$	$0.2 \cdot 10^{-5}$	8	0.04	0.09
25	$NiCl_2$	$0.1 \cdot 10^{-5}$	10	0.03	0.06

(X) oxidation with air

Example 26

The oxidation of saccharose is carried out in a 150 ml autoclave, provided with mechanical stirrer, at the oxygen pressure of 1.0 MPa in the presence of 100 ml of water, 0.17 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($1 \cdot 10^{-2}$ M), 8 g NaOH (2.0 M) at the temperature of 75°C; saccharose concentration 20% by weight.

Example 27

The procedure of Example 26 was repeated with the use of maize starch at a concentration of 20% wt.

Examples 28-29

The procedures of examples 26 and 27 were repeated at the oxygen pressure of 0.1 MPa. The data of examples 26-29 are summarised in Table 6.

TABLE 6

Examples	Substrate of oxidation	P_{O_2} MPa	Reaction time, h	hydroxyacids concentration*
26	Saccharose	1.0	3.0	1.9
27	Saccharose	0.1	10.0	1.7
28	Maize starch	1.0	4.0	1.8
29	Maize starch	0.1	20.0	1.6

* Calculated for 1 COOH-group

Example 30

In a 22 l autoclave (provided with a stirring system and thermostatic jacket), 10 l of distilled water, 2 kg of maltodextrin (medium molecular weight of about 10^5), 12.5 g of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, 1.383 kg NaOH pellets were added. 5 MPa of air were charged and the temperature was raised to 70°C. During 16 hours of reaction, oxygen-exhausted air was renewed four times (every about three hours). The reaction mixture was cooled to room temperature. The final pH was equal to 9. Water was removed in a spray drier equipment obtaining 2.8 kg of a white powder. The results are summarised in Table 7.

Examples 31-32

The procedure of example 20 was repeated using commercial maize starch and starch hydrolyzate (medium molecular weight of about $1 \cdot 10^3$). Conditions and results obtained in Examples 21-22 are summarised in Table 7.

TABLE 7

OXIDATION OF STARCH AND STARCH HYDROLYZATES UNDER PRESSURE WITH AIR (5 MPa)					
Example	substrate	mmoles of NaOH/Gl. units	T°C	React. time (h)	hydroxyacid conc.
30	Maltodextrin	2.8	70	16	2.34M
31	Hydrolyzed Starch	2.8	65	12	2.47M
32	Starch	2.8	75-80	16	2.21M

Table 8 summarises the preferred conditions for oxidation of different mono- and di-saccharides, maize starch and maize starch hydrolyzates with references to aqueous solutions having a concentration of the substrate of 10% wt.

TABLE 8

PREFERRED CONDITIONS FOR CARBOHYDRATES OXIDATION (AQUEOUS SOLUTIONS 10% W/W)			
Carbohydrate	T°C	Concentration of base, NaOH, M	Catalyst concentration $\text{Cu(II)} \cdot 10^3$, M
D - Mannitol	30 + 50	0.05 ÷ 0.10	3.0

TABLE 8 (continued)

PREFERRED CONDITIONS FOR CARBOHYDRATES OXIDATION (AQUEOUS SOLUTIONS 10% W/W)			
Carbohydrate	T°C	Concentration of base, NaOH, M	Catalyst concentration Cu(II) · 10 ³ , M
D - Sorbitol	40 + 60	0.10 + 0.15	5.0
Dulcitol	40 + 60	0.05 + 0.10	5.0
L-Arabinose	30 + 50	0.05	10.0
D - Glucose	30 + 50	0.05	5.0
L - Rhamnose	40 + 60	0.20 + 0.50	5.0
D - Lactose	40 + 50	0.10 + 0.20	5.0
D - Maltose	30 + 60	0.05 + 0.10	10.0
Saccharose	60 + 80	0.20 + 0.40	5.0
Hydrolysed Maize starch, M.W. 10 ³ -10 ⁵	60 + 70	0.10 + 0.30	20.0
Maize starch	70 + 80	0.10 + 0.20	10.0

Claims

1. A method for the production of hydroxyacids from carbohydrates by catalytic oxidation with an oxygen-containing gas, in an alkaline medium, characterised in that the oxidation is carried out by homogeneous catalysis in the presence of a catalytic amount of an ion of a transition metal selected from the group consisting of Cu, Cr, Co, Ni, Fe, V, Ti, Mn and mixtures thereof, wherein the carbohydrate is first dissolved or dispersed in an aqueous medium with the addition of a catalytic amount of said metal ion and then an amount of base is added such as to maintain the pH in alkaline conditions throughout the oxidation reaction and through said medium molecular oxygen is fed provided that when the reaction is carried out in the presence of Cu, Co, Ni, or Fe ions the aqueous medium does not contain any amine compound that acts as a ligand for such ions.
2. A method according to claim 1 wherein the reaction medium is maintained in alkaline conditions by addition of an alkaline agent selected from the group consisting of alkali, alkaline-earth metal hydroxides, amines such as ethylamine, diethylamine, triethylamine, ammonia and quaternary ammonium hydroxides.
3. A method according to any one of the preceding claims wherein the carbohydrate is present in the reaction medium in the amount of from 5 to 50% wt and the metal ion molar concentration is from 0.01 · 10⁻² to 4 · 10⁻² M.
4. A method according to any one of the preceding claims wherein the oxidation reaction is carried out at a temperature of from 25 to 100°C with oxygen partial pressure of from 0.02 to 10 MPa.
5. A method according to any one of the preceding claims wherein the carbohydrate subjected to oxidation is selected from the group consisting of cellulose, starch, starch hydrolyzates, dextrans, dextrans, mono-, and di-saccharides.
6. A method according to claim 1, wherein the carbohydrate is selected from the group consisting of cellulose, starch, starch hydrolyzates, dextrans and dextrans and the reaction is carried out with addition of base in the amount such as to maintain a pH of from 8 to 13, at a temperature of from 50 to 80°C.
7. A method according to claim 1, wherein the carbohydrate is selected from the group consisting of maltose, sac-

charose, reduced monosaccharides and the reaction is carried out with the addition of a base in the amount such as to maintain a pH of from 7.5 to 12, at a temperature of from 25 to 80°C.

8. The use of the product obtainable by the process of claim 7 as a binder for paper.
9. The use of the product obtainable by the oxidation of mono- and di-saccharides in the process of claim 1 as a corrosion-inhibitor or food preservative.
10. The use of the product as obtainable by the process of claim 7 as a builder for detergents.
11. A product of oxidation of a carbohydrate selected from the group consisting of cellulose and dextrans, characterised in that it is obtainable by catalytic oxidation with an oxygen containing gas in an alkaline medium in the presence of a catalytic amount of an ion of a transition metal selected from the group consisting of Cu, Cr, Ni, Fe, V, Ti, Mn and mixtures thereof, according to the conditions set forth in claim 1.

Patentansprüche

1. Verfahren zur Herstellung von Hydroxysäuren aus Kohlenhydraten durch katalytische Oxidation mit einem Sauerstoff enthaltenden Gas in einem alkalischen Medium, dadurch gekennzeichnet, daß die Oxidation durch homogene Katalyse in Gegenwart einer katalytischen Menge eines Ions eines Übergangsmetalls, ausgewählt aus der Gruppe, bestehend aus Cu, Cr, Co, Ni, Fe, V, Ti, Mn und Gemischen davon, ausgeführt wird, wobei das Kohlenhydrat zuerst in einem wässrigen Medium unter Zugabe einer katalytischen Menge des Metallions gelöst oder dispergiert wird und anschließend eine Menge einer Base so zugegeben wird, daß der pH-Wert während der gesamten Oxidationsreaktion im Alkalischen gehalten wird und durch das Medium molekularer Sauerstoff geleitet wird, mit der Maßgabe, daß wenn die Reaktion in Gegenwart von Cu-, Co-, Ni- oder Fe-Ionen ausgeführt wird, das wässrige Medium keine Aminverbindung enthält, die als Ligand für solche Ionen wirkt.
2. Verfahren nach Anspruch 1, wobei das Reaktionsmedium durch Zugabe eines alkalischen Mittels, ausgewählt aus der Gruppe, bestehend aus Alkali-, Erdaalkalimetallhydroxiden, Aminen, wie Ethylamin, Diethylamin, Triethylamin, Ammoniak und quaternären Ammoniumhydroxiden, unter alkalischen Bedingungen gehalten wird.
3. Verfahren nach einem der vorangehenden Ansprüche, wobei das Kohlenhydrat im Reaktionsmedium in der Menge von 5 bis 50 Gewichtsprozent vorliegt und die molare Metallionen-Konzentration $0,01 \times 10^{-2}$ bis 4×10^{-2} M beträgt.
4. Verfahren nach einem der vorangehenden Ansprüche, wobei die Oxidationsreaktion bei einer Temperatur von 25 bis 100°C mit einem Sauerstoffpartialdruck von 0,02 bis 10 MPa ausgeführt wird.
5. Verfahren nach einem der vorangehenden Ansprüche, wobei das zu oxidierende Kohlenhydrat ausgewählt ist aus der Gruppe, bestehend aus Zellulose, Stärke, Stärkehydrolysaten, Dextrinen, Dextranen, Mono- und Disacchariden.
6. Verfahren nach Anspruch 1, wobei das Kohlenhydrat ausgewählt ist aus der Gruppe, bestehend aus Zellulose, Stärke, Stärkehydrolysaten, Dextrinen und Dextranen, und die Reaktion unter Zugabe von Base in einer solchen Menge, daß der pH-Wert von 8 bis 13 gehalten wird, bei einer Temperatur von 50 bis 80°C ausgeführt wird.
7. Verfahren nach Anspruch 1, wobei das Kohlenhydrat ausgewählt ist aus der Gruppe, bestehend aus Maltose, Saccharose, reduzierten Monosacchariden, und die Reaktion unter Zugabe einer Base in einer Menge, daß der pH-Wert von 7,5 bis 12 gehalten wird, bei einer Temperatur von 25 bis 80°C ausgeführt wird.
8. Verwendung des durch das Verfahren von Anspruch 7 erhältlichen Produkts als Bindemittel für Papier.
9. Verwendung des durch die Oxidation von Mono- und Disacchariden in dem Verfahren von Anspruch 1 erhältlichen Produkts als Korrosionsinhibitor oder Lebensmittelkonservierungsstoff.
10. Verwendung des durch das Verfahren von Anspruch 7 erhältlichen Produkts als Waschmittelbuilder.
11. Oxidationsprodukt eines Kohlenhydrats, ausgewählt aus der Gruppe, bestehend aus Zellulose und Dextranen,

dadurch gekennzeichnet, daß es durch katalytische Oxidation mit einem Sauerstoff enthaltenden Gas in einem alkalischen Medium in Gegenwart einer katalytischen Menge eines Ions eines Übergangsmetalls, ausgewählt aus der Gruppe, bestehend aus Cu, Cr, Ni, Fe, V, Ti, Mn und Gemischen davon, gemäß den in Anspruch 1 angeführten Bedingungen erhältlich ist.

5

Revendications

1. Procédé de fabrication d'hydroxyacides à partir de carbohydrates par oxydation catalytique par un gaz contenant de l'oxygène, en milieu alcalin, caractérisé en ce que l'oxydation est exécutée par catalyse homogène en présence d'une quantité catalytique d'un ion d'un métal de transition choisi dans le groupe formé par Cu, Cr, Co, Ni, Fe, V, Ti, Mn et leurs mélanges, dans lequel le carbohydrate est abord dissous ou dispersé dans un milieu aqueux avec addition d'une quantité catalytique de l'ion métallique, puis une quantité d'une base est ajoutée afin que le pH soit maintenu dans des conditions alcalines pendant toute la réaction d'oxydation, et de l'oxygène moléculaire est transmis dans ce milieu dans des conditions telles que, lorsque la réaction est exécutée en présence d'ions Cu, Co, Ni ou Fe, le milieu aqueux ne contient pas de composés sous forme d'une amine formant un ligand pour ces ions.
2. Procédé selon la revendication 1, dans lequel le milieu de la réaction est maintenu dans les conditions alcalines par addition d'un agent alcalin choisi dans le groupe constitué par les hydroxydes alcalins et alcalino-terreux, les amines telles que l'éthylamine, la diéthylamine et la triéthylamine, l'ammoniaque et les hydroxydes d'ammonium quaternaire.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le carbohydrate est présent dans le milieu réactionnel en quantité comprise entre 5 et 50 % en poids, et la concentration molaire des ions métalliques est comprise entre $0,01 \cdot 10^{-2}$ et $4 \cdot 10^{-2}$ M.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la réaction d'oxydation est réalisée à une température comprise entre 25 et 100 °C, avec une pression partielle d'oxygène comprise entre 0,02 et 10 MPa.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le carbohydrate soumis à l'oxydation est choisi dans le groupe formé par la cellulose, l'amidon, les hydrolysats d'amidon, les dextrines, les dextrans, les oses et les diholosides.
6. Procédé selon la revendication 1, dans lequel le carbohydrate est choisi dans le groupe qui est formé par la cellulose, l'amidon, les hydrolysats d'amidon, les dextrines et les dextrans, et la réaction est réalisée avec addition d'une d'une base en quantité telle que le pH est maintenu entre 8 et 13 et à une température comprise entre 50 et 80 °C.
7. Procédé selon la revendication 1, caractérisé en ce que le carbohydrate est choisi dans le groupe formé par le maltose, la saccharose, et les oses réduits, et la réaction est exécutée avec addition d'une base en quantité telle que le pH est maintenu entre 7,5 et 12, à une température de 25 à 80 °C.
8. Application du produit obtenu par le procédé de la revendication 7 à la formation d'un liant pour le papier.
9. Application du produit obtenu par oxydation d'oses et de diholosides suivant le procédé de la revendication 1 à un inhibiteur de corrosion et un agent de conservation alimentaire.
10. Application du produit qui peut être obtenu par le procédé de la revendication 7 à un agent destiné à des détergents.
11. Produit d'oxydation d'un carbohydrate choisi dans le groupe formé de la cellulose et des dextrans, caractérisé en ce qu'il peut être obtenu par oxydation catalytique d'un gaz contenant de l'oxygène en milieu alcalin en présence d'une quantité catalytique d'un ion d'un métal de transition choisi dans le groupe formé par Cu, Cr, Ni, Fe, V, Ti, Mn et leurs mélanges, dans les conditions indiquées dans la revendication 1.

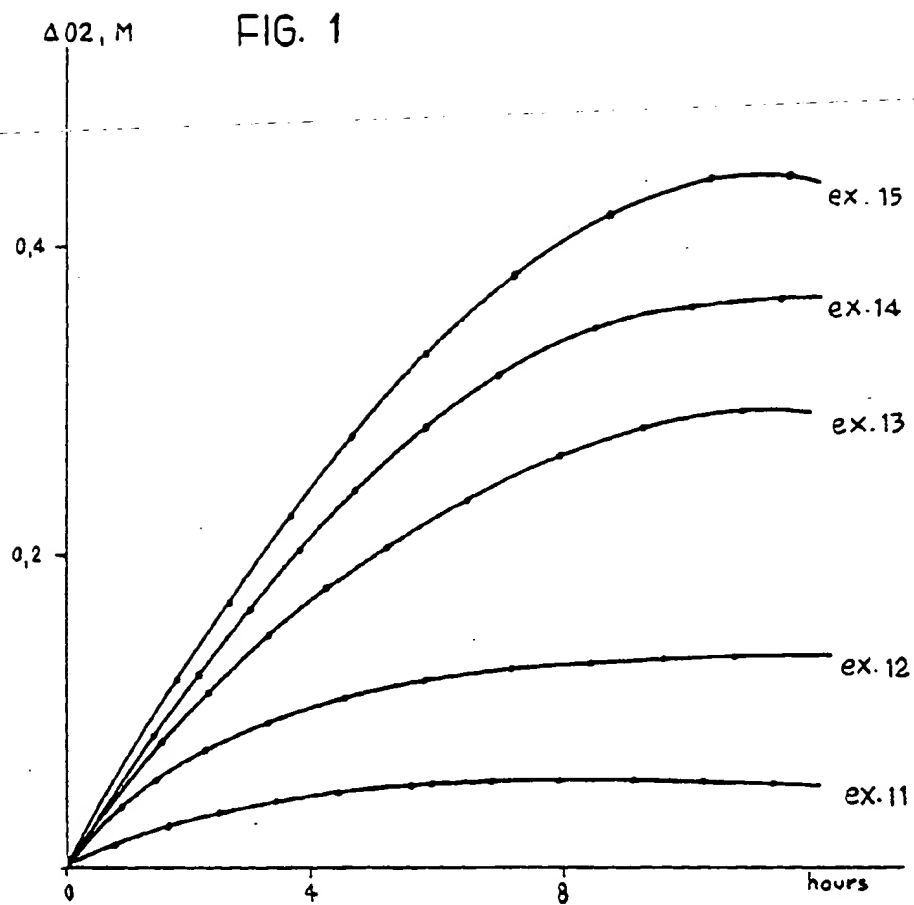


Fig. 1 Kinetic curves of oxygen uptake during cellulose oxidation in the presence of different amounts of NaOH (examples 11-15)

$CuSO_4 \cdot 5H_2O = 1 \cdot 10^{-2}$ M, cellulose = 100 g/l, 80°C

$P_{O_2} = 0,1$ MPa

Example	$[NaOH]_0$, N
11	0,1
12	0,3
13	0,5
14	0,7
15	0,9

FIG. 2

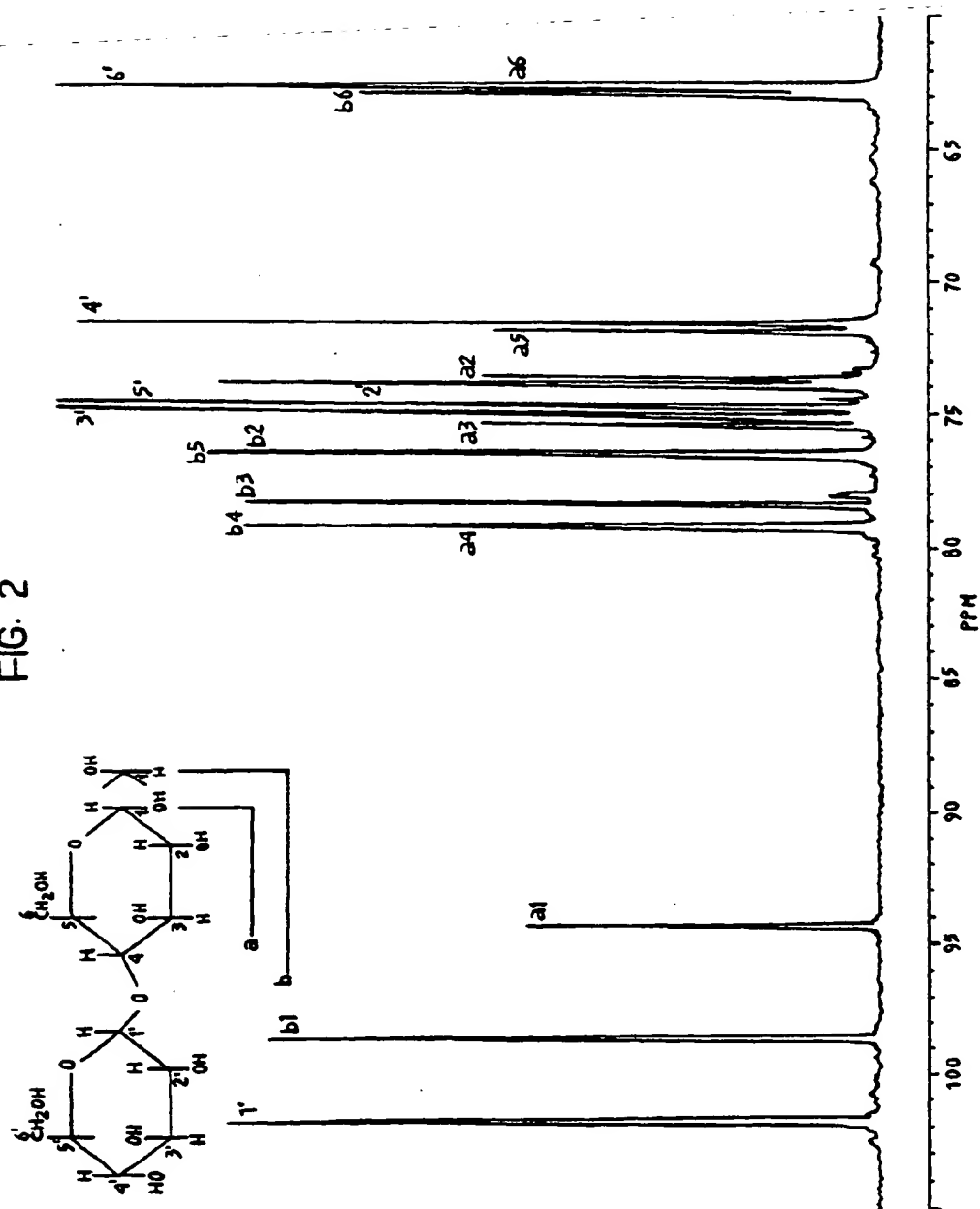
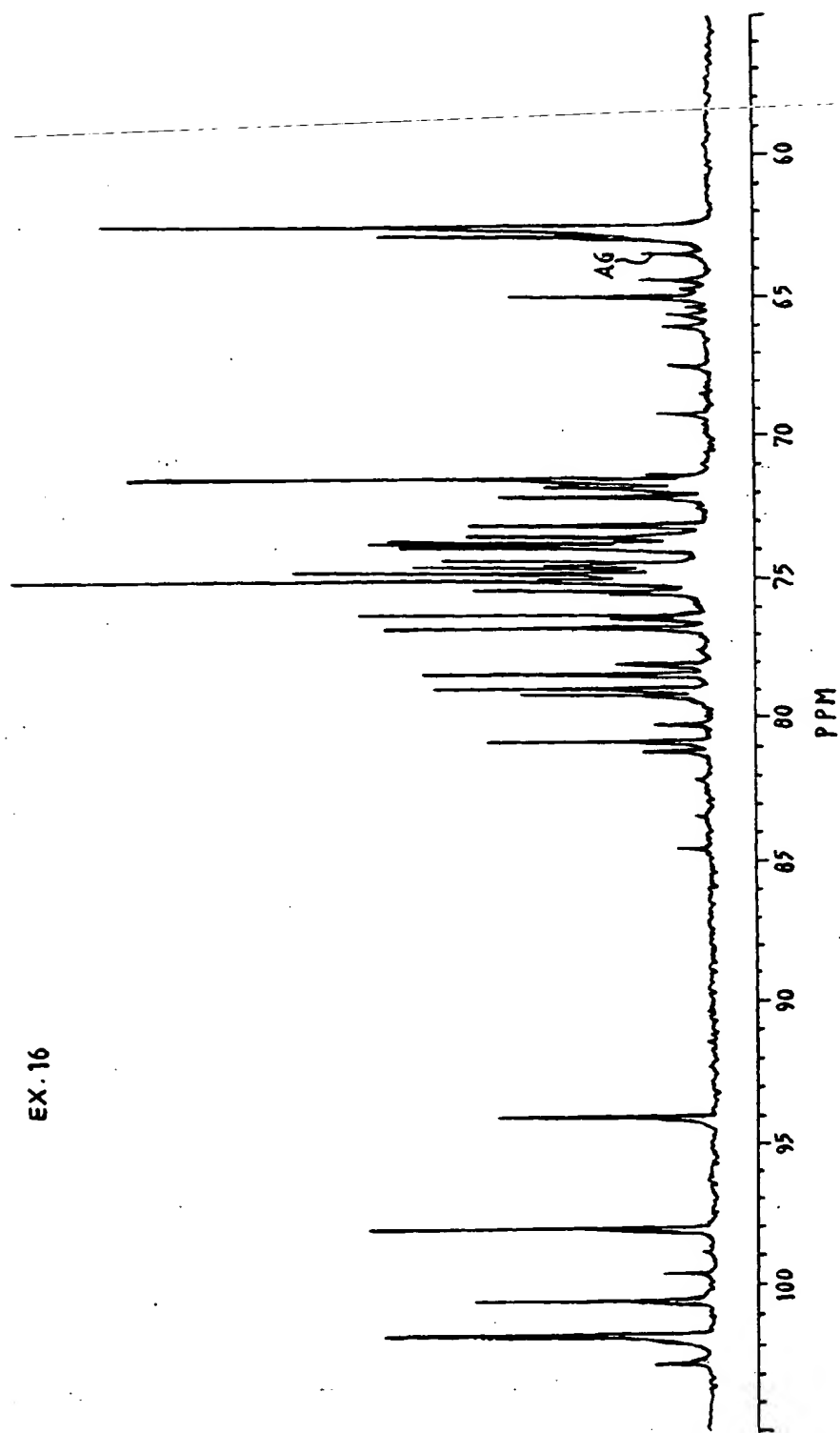


FIG. 3
EX. 16



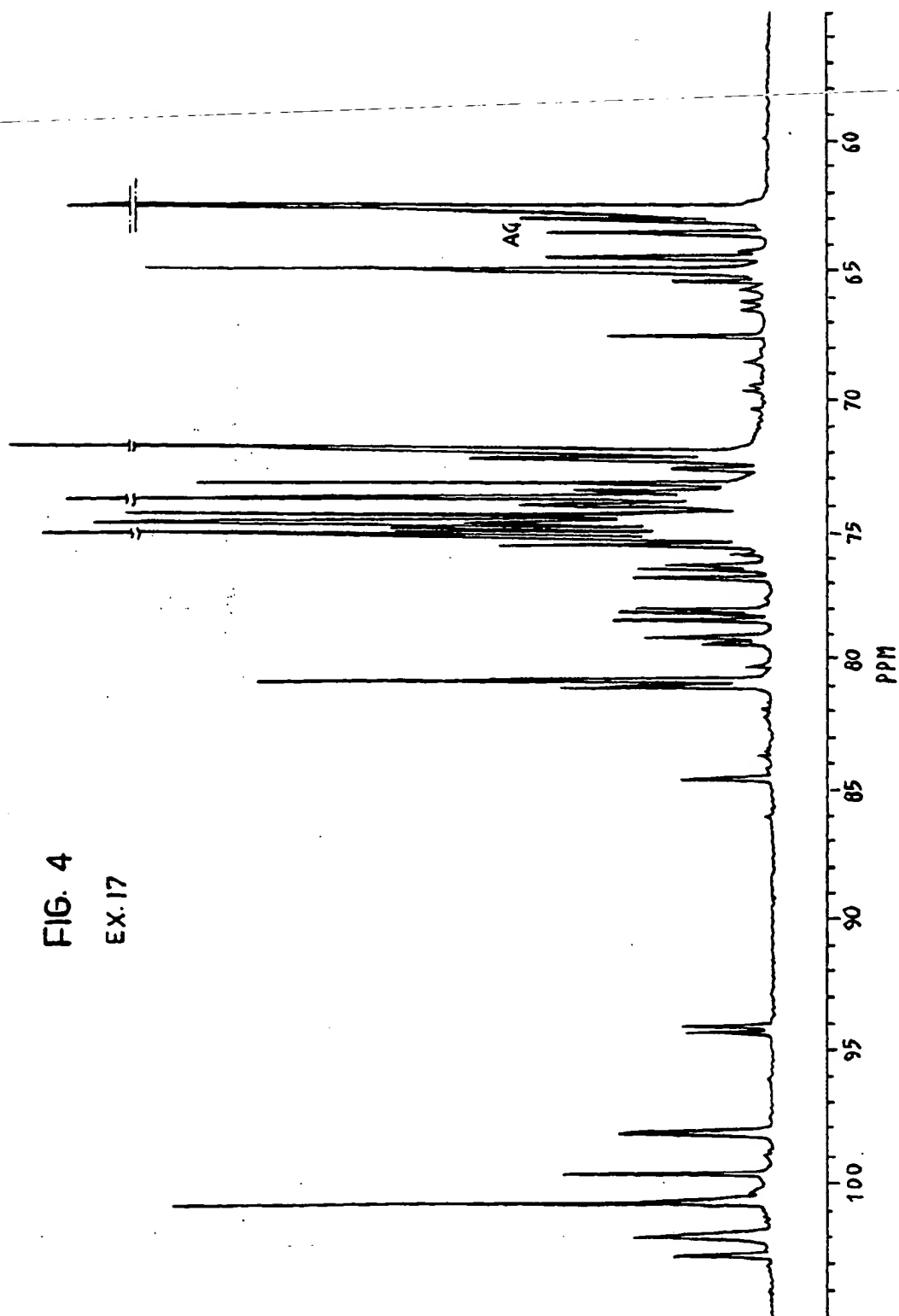


FIG. 5
EX. 18

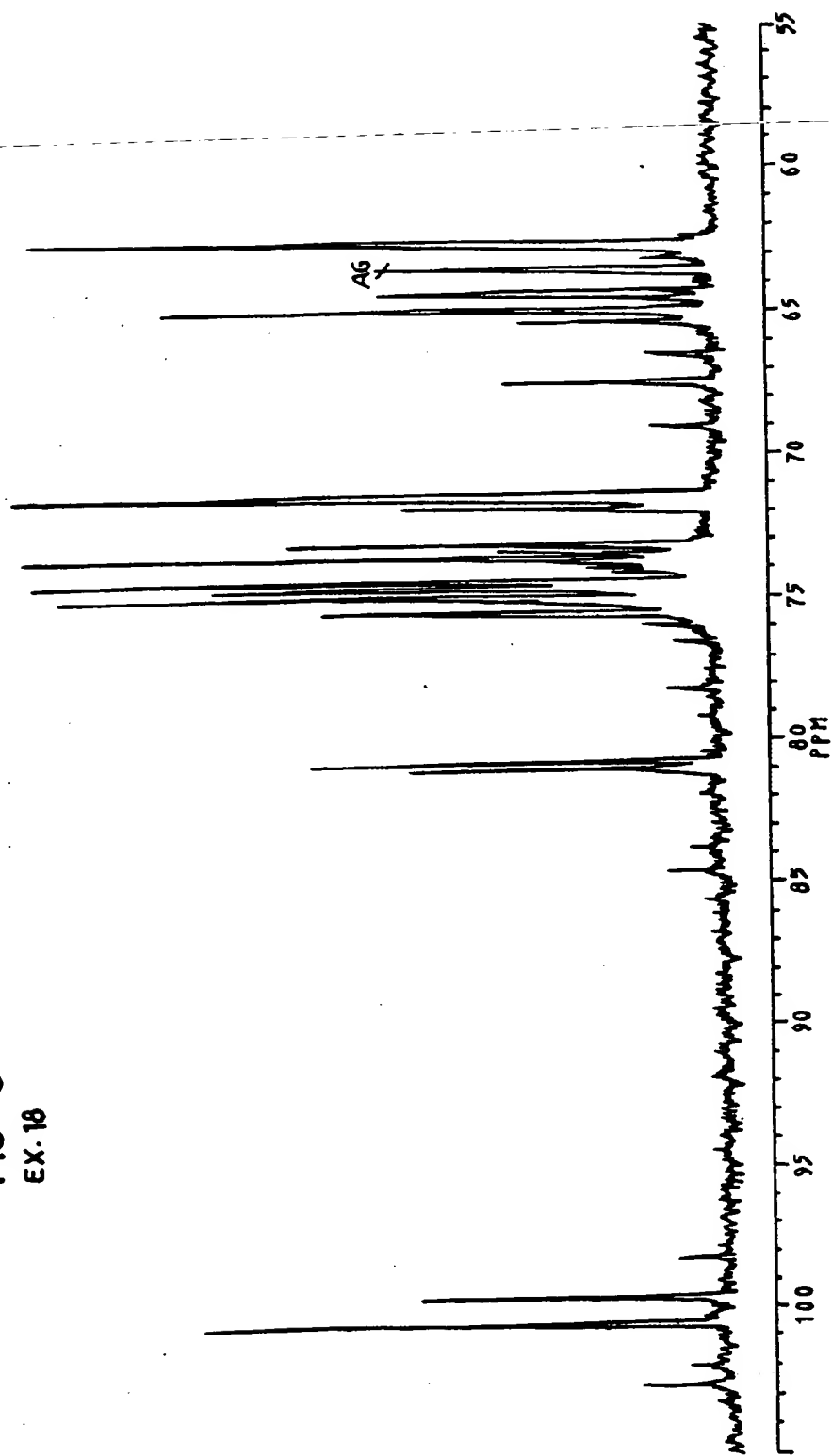


FIG. 6
EX. 19

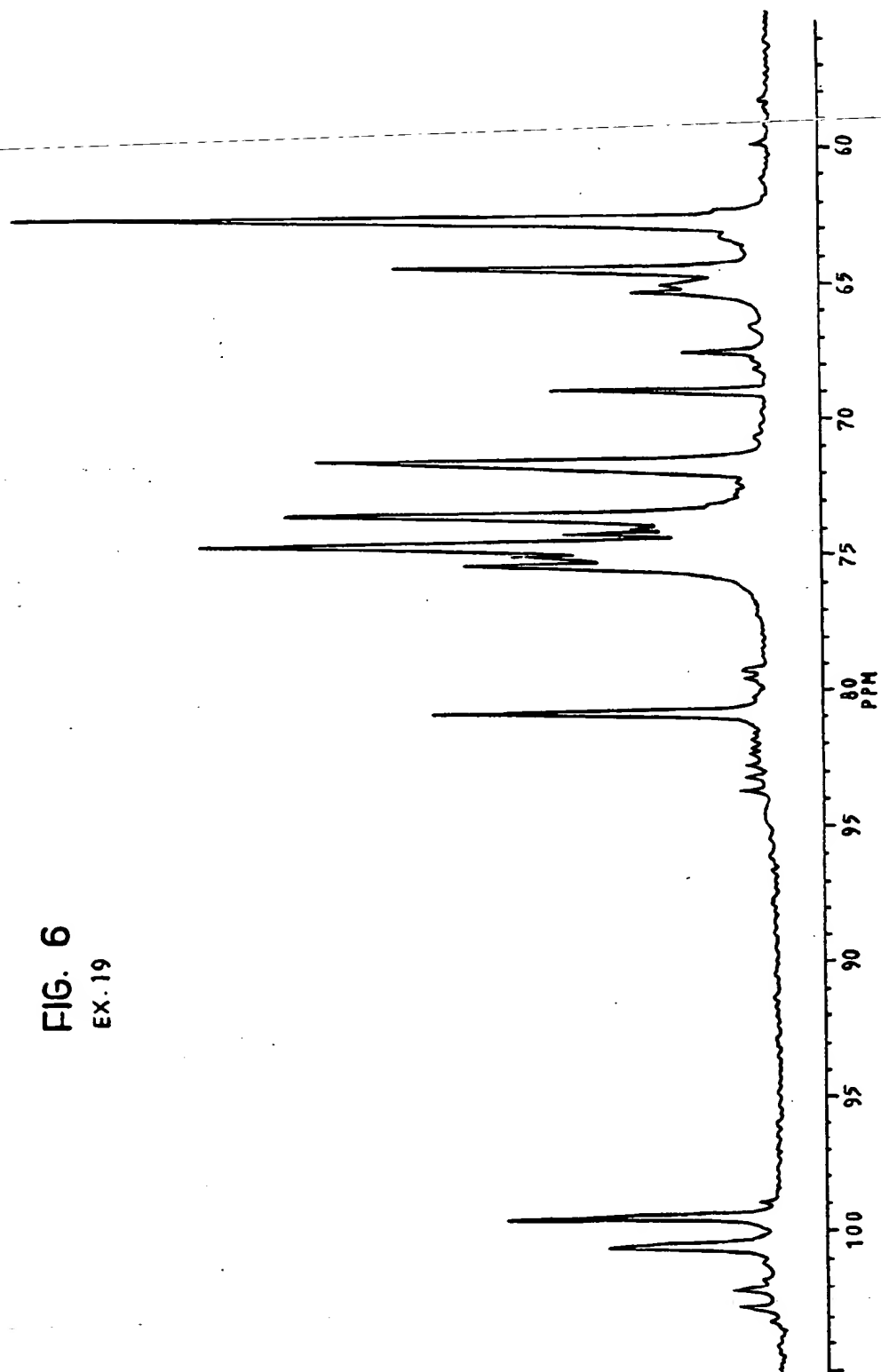


FIG. 7

